REPORT 53

SWEEP

SOIL AND WATER

ENVIRONMENTAL

ENHANCEMENT PROGRAM

PAMPA

PROGRAMME D'AMELIORATION

DU MILIEU PEDOLOGIQUE

ET AQUATIQUE

Canada

Ontario

SWEEP

is a $30 million federal-provincial agreement, announced May 8, 1986, designed to improve soil and water quality in southwestern Ontario over the next five years.

PURPOSES

There are two interrelated purposes to the program; first, to reduce phosphorus loadings in the Lake Erie basin from cropland run-off; and second, to improve the productivity of southwestern Ontario agriculture by reducing or arresting soil erosion that contributes to water pollution.

BACKGROUND

The Canada-U.S. Great Lakes Water Quality Agreement called for phosphorus reductions in the Lake Erie basin of 2000 tonnes per year. SWEEP is part of the Canadian agreement, calling for reductions of 300 tonnes per year — 200 from croplands and 100 from industrial and municipal sources.

PAMPA

est une entente fédérale-provinciale de 30 millions de dollars, annoncée le 8 mai 1986, et destinée à améliorer la qualité du sol et de l'eau dans le Sud-ouest de l'Ontario.

SES BUTS

Les deux buts de PAMPA sont: en premier lieu de réduire de 200 tonnes par an d'ici 1990 le déversement dans le lac Erie de phosphore provenant des terres agricoles, et de maintenir ou d'accroître la productivité agricole du Sud-ouest de l'Ontario, en réduisant ou en empêchant l'érosion et la dégradation du sol.

SES GRANDES LIGNES

L'entente entre le Canada et les États-Unis sur la qualité de l'eau des Grands Lacs prévoyait de réduire de 2 000 tonnes par an la pollution due au phosphore dans le bassin du lac Erie. PAMPA fait partie de cette entente qui réduira cette pollution de 300 tonnes par an — 200 tonnes provenant des terres agricoles et 100 tonnes provenant de sources industrielles et municipales.

100-05247/

TECHNOLOGY EVALUATION AND DEVELOPMENT SUB-PROGRAM

PHOSPHORUS MOVEMENT IN SOIL AS A FUNCTION OF PHOSPHORUS SOLUBILITY AND REACTIVITY

FINAL REPORT

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EXECUTIVE SUMMARY

To investigate the possible role of crop residues on the release of soil phosphorus and its effect on crop growth, a series of three experiments were performed. An acidic soil (Welland Series), pH 5.3, from the Niagara region of southern Ontario was limed to pH's 6.4 and 7.5 by addition of two rates of lime, $CaCO_3$. Corn residues were either added directly to the soil surface or were incorporated into the soil. The experiment consisted of nine treatments;- three soil treatments - control, surface applied residue and incorporated residue, and three pH values - 5.3, 6.4, 7.5. Barley was grown in the various soils in a greenhouse. The plants were harvested at two different growth periods, corresponding to Feeke's stages 3 and 6. Both plant and soil analyses were performed.

There were differences in the yield of barley between the control soil and the two residue treatments. These differences in yield however were not significant at the first harvesting period. Final yields at the later harvesting were significantly lower in the control than in the two residue treatments at the two lower pH values but the effect of the residue treatments on final barley yields disappeared in the soil limed to a pH of 7.5.

The increased yield for the residue treatments did not appear to be due to an increased content of tissue phosphorus. The increased plant yields appeared to be more directly related to increased tissue potassium content at the earlier date of harvesting and to an increased tissue nitrogen content at the later harvesting date.

The increased yields also corresponded to increased soluble carbon contents in the extracted soil solutions and therefore it is possible that the degradation of the corn residues either at the soil surface or directly incorporated into the soil released soluble nitrogen and potassium, in addition to soluble phosphorus. Although there was some evidence for increased soluble phosphorus contents in the extracted soil solutions these increases were not significant.

In a second experiment, the soils with the three different pH values were incubated with incorporated corn or alfalfa residue over a period of forty eight days. At various time intervals the soil solution were extracted and analyzed for soluble organic carbon and phosphorus.

Incubation with either corn and alfalfa residues lead to an increase in soluble organic carbon, soluble total phosphorus and ortho-phosphate. The maximum amounts of each of the constituents occurred at after two to three weeks, with contents of the constituents being released over a longer time period for alfalfa than for corn. Because of uncertainties in the exact nature of total phosphorus measured by the ICP-AES technique, it was not clear whether this increase in phosphorus content is due to the release of mineral-bound phosphorus or due to an increase in organic phosphorus. An automated procedure for determining both inorganic and organic forms of soluble phosphorus was developed in the latter stages of this work - see Appendix I.

In the third experiment, the soils were shaken with phosphate in the presence and absence of different naturally occurring organic acids. It was shown that retention of phosphorus was less in the presence of these acids and that those organic acids that form strong bonds with the surfaces of soil particles were the most effective in reducing specific adsorption of phosphate.

This study has shown that there is an increase on crop yield if soils at three different pH's are amended with crop residues either applied at the soil surface or incorporated into the soil. Incubation of the soils with either corn or alfalfa residues increases the amount of soluble phosphorus in the soil solution after about two to three weeks of incubation. With increased time however the content of soluble phosphorus decreases. This increase in soluble phosphorus is probably due in part to release of inorganically and organically bound phosphorus from the crop residues and, as the final part of the study has shown, to release of soil bound phosphorus by the increased concentration of released organic acids.

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LITERATURE REVIEW

Introduction

One of the two primary objectives of the SWEEP program is to reduce significantly the phosphorus loading of Lake Erie from non-point agricultural sources. As a result of soil erosion, the major form of phosphorus entering the lake is phosphorus adsorbed to soil particles, with soluble phosphorus of much lesser concern. The efficiency of plant uptake of applied phosphorus is reduced significantly as a result of adsorption and consequently relatively large applications of phosphorus to agricultural soils have to be made to satisfy crop requirements.

The use of no- or minimum tillage practices is now widely advocated in Ontario to reduce the extent of soil erosion and subsequently lessen the phosphorus loading of the Great lakes. One of the consequences of these tillage practices is the reduced rate of decomposition of crop residues and an increased content of decomposition products in the soil solution. These products are largely composed of low molecular weight aliphatic and aromatic organic acids and increased contents of these acids can effect the adsorption of applied phosphorus and also the uptake of phosphorus by crops. Because phosphate and organic acids will compete for the same adsorption sites on soil particles, an increased content of these acids will lessen the extent of adsorption and increase the amount of phosphorus in the soil solution, thus increasing the efficiency of phosphorus utilization.

The effects of crop residues and other sources of organic carbon on the adsorption of phosphorus by soil particles has not as yet been fully evaluated. Observations on the effects of crop residues on phosphorus mobility do however indicate decreased phosphorus adsorption and increased solution phosphorus when the rate of residue decomposition is changed by various tillage practices (Singh and Jones, 1976; Dick, 1983; Easterwood, 1987).

The interactions between high contents of organic matter input into soil and the availability of soil phosphorous have been demonstrated for various crops under no-till or minimum-till conditions (McDowell and McGregor, 1984; Langdale *et al.*, 1985). Similarly, the accumulation at the soil surface of a crop residue cover from previous cropping has been shown to increase the soil test value for phosphorus (Sharpley and Smith, 1989). Observations of this nature have also been made on changes in the availability of soil phosphorous after the application of liquid manures to soil (Sharpley *et al.*, 1984; Meek *et al.*, 1979; Meek *et al.*, 1982). Results from these various studies have shown increases in both organically and inorganically bound soil phosphorus.

To be able to predict the effects of organic matter additions on phosphorus solubility and reactivity it is necessary to develop mathematical models that incorporate estimates of organic matter decomposition, such as that proposed by Stroo *et al.* (1989), in addition to models that can describe the adsorption of phosphorus by soils. Examples of the latter are surface complexation models, such as the constant capacitance and triple layer models, that incorporate the formation of inner-sphere complexes at the surface of soil particles with changes in the charge characteristics of the soil as a function of pH. The great advantage of tested mathematical models is that the results from such models can be applied to a wide range of soils without necessarily conducting extensive field trials on a multitude of different, but similar, soils.

It should be possible to calculate the changes in the content of both adsorbed phosphorus and soluble phosphorus as a result of various tillage practices. This calculation will be possible by combining a crop residue decomposition model with a surface complexation model. A knowledge of these parameters will enable predictions to be made on changes to the soil test value for phosphorus, on the efficiency of phosphorus uptake by crops and on the amount of phosphorus adsorbed on potentially erodible soil particles.

Forms of phosphorus in soil

Although much is known about the inorganic chemistry of soil phosphorous (Larsen, 1969) and its possible organic forms (Dalal, 1977), very few studies have been conducted on the interactions between additions of organic matter to soil and the transport mechanisms of soil phosphorous. To understand the chemistry of these interactions more fully it is necessary to know both the possible forms of phosphorous in soil and the mechanisms involved in phosphorous retention and release.

The various forms of phosphorous found in soils may be summarized as follows:-

- Inorganic and organic forms in the soil solution - these include the ions $H_2PO_4^-$ and HPO_4^{2-}, as well as ion pairs, such as $CaHPO_4^\circ$ (Stumm and Morgan, 1981).

$H_3PO_4 \rightleftarrows H_2PO_4^- + H^+$	$pK_{a1} = 2.1$
$H_2PO_4^- \rightleftarrows HPO_4^{2-} + H^+$	$pK_{a2} = 7.2$
$HPO_4^{2-} \rightleftarrows PO_4^{3-} + H^+$	$pK_{a3} = 12.3$
$Ca^{2+} + HPO_4^{2-} \rightleftarrows CaHPO_4$	$pK_a = 2.7$

- Mineral precipitates - these include the calcium containing phosphates, such as dicalcium phosphate, $CaHPO_4.2H_2O$, and hydroxyapatite, $Ca_5(PO_4)_3OH$, as well as Al- and Fe-containing phosphate minerals, such as variscite and vivianite (Talibudeen, 1981).

	pK_{so}
$CaHPO_4 \rightleftarrows Ca^{2+} + HPO_4^{2-}$	6.6
$Ca_8H_2(PO_4)_6 \rightleftarrows 8Ca^{2+} + 6PO_4^{3-} + 2H^+$	46.9
$AlPO_4.2H_2O \rightleftarrows Al^{3+} + PO_4^{3-} + 2H_2O$	21
$FePO_4.2H_2O \rightleftarrows Fe^{3+} + PO_4^{3-} + 2H_2O$	26

- Specifically adsorbed phosphate on the surfaces of variable charge minerals, such as goethite, allophane and ferrihydrite (Goldberg and Sposito, 1984).

$\equiv Me\text{-}OH^\circ + H_3PO_4 \rightleftarrows \equiv Me\text{-}O\text{-}PO(OH)_2 + H_2O$	$pK_{L1}^{int} = -10.59$
$\equiv Me\text{-}OH^\circ + H_3PO_4 \rightleftarrows \equiv Me\text{-}O\text{-}PO_2(OH)^- + H_2O$	$pK_{L2}^{int} = -5.00$
$\equiv Me\text{-}OH^\circ + H_3PO_4 \rightleftarrows \equiv Me\text{-}O\text{-}PO_3^{2-} + H_2O$	$pK_{L3}^{int} = 1.16$

- Soluble organic phosphorous compounds, such as the inositol phosphates, e.g. phytic acid, derived from plant residues (Stevenson 1982).

The organic chemistry of crop residues and liquid manure

An average composition of the constituents in plant material is usually from 60 to 80% hemicellulose, from 20 to 35% lignin and less than 10% proteins. These polymeric plant materials degrade in soils to give sugars, phenolic acids and amino acids respectively. Of particular importance in influencing the chemistry of soil phosphorus from both crop residues and manures are the low molecular weight aliphatic and aromatic acids produced during biomass degradation. The aliphatic acids are formed principally during the breakdown of the hemicellulose carbohydrates, whereas the aromatic acids form during the breakdown of lignin.

Amongst the short chain aliphatic acids identified in crop residues and manures are formic, acetic, propionic, butyric, iso-valeric and oxalic acids (Stevenson 1982; Lynch 1985). A variety of aromatic acids have also been identified in decomposing vegetation and include p-hydroxybenzoic, vanillic, p-coumaric, ferulic, protocatechuic, syringic, gallic and salicylic acids (Whitehead, Dibb and Hartley 1982; Jalal and Read, 1983). These acids are important competing anions for adsorption sites with phosphorus on the surfaces of soil particles.

Mechanisms of phosphorus transport in presence of organic matter

The addition of organic residues to soil may affect the solubility of phosphorus through a number of possible mechanisms. These mechanisms may include the following:-

- An increase in the amount of organically-bound phosphorus in the soil solution through interaction between the organic residues, and/or their metabolites, with native soil phosphorus.
- An increase in the content of total dissolved inorganic phosphorus through the formation of weak ion-pairs with constituents within the residues.
- The displacement of specifically adsorbed phosphorus from the surfaces of variable charged minerals by competition with surface-complexant organic ligands, such as acetate or salicylate.
- A decrease in soil pH resulting from the metabolism of organic residues which leads to a concomitant increase in dissolved inorganic phosphorus.

EXPERIMENTS

1. Evaluation of the Role of Crop Residues on Plant Uptake of P.

Experimental design

A greenhouse experiment was conducted to evaluate the effects of crop residues on the uptake of soil phosphorus by barley, on the yield of barley and on the changes to the various forms of P that might be available to plants. Various rates of crop residues were added to a representative agricultural soil from Ontario:- the Welland clay soil. The initial pH of the soil was 5.3 and this value was raised by

addition of two rates of lime ($CaCO_3$) to give final pH's of 6.4 and 7.5. The content of both phosphorus and other major and minor elements in the shoots and roots of the harvested barley were determined in the Plant Analysis Laboratory at the University of Guelph and the uptake of phosphorus by barley was assessed.

1 soil:- Welland clay (Niagara)

3 pH's:
1) 5.3 - 2.0 g/kg of $CaCO_3$
2) 6.4 - 5.0 g/kg of $CaCO_3$
3) 7.5 - 12.0 g/kg of $CaCO_3$

1 Residue type:- Corn - "1/2-1" size residue

2 Types of residue placement:
1) Surface placement
2) Incorporated

1 Rate of residue addition:- 22.7 g corn residue/8" pot

2 Sampling dates:
1) Stage 3 (Feeke's scale)
2) Stage 6 (Feeke's scale)

Crop grown:- Barley (Rodeo variety)

All treatments were performed in triplicate

Materials and methods

The soil used for the greenhouse study was air-dried and passed through a 5 cm stainless steel sieve. Three kilograms of soil were mixed well with the two additions of $CaCO_3$ and the pots placed in 4 L plastic pots lined with polyethylene sheets. All the soils were incubated at a moisture content of 30% (w/w, 94% of the field capacity) for four weeks in a greenhouse at a day temperature of 26°C and night temperature of 19°C. The pots were not covered so that they could equilibrate with the atmosphere. Water was added to keep the moisture content constant. This incubation took one month. The soil samples were then air-dried to a moisture content of about 20% and thoroughly mixed with $Ca(H_2PO_4)_2.H_2O$ as a source of P in a solid state and returned to the pots. Nutrient solutions were then added to the pots as follows:-

N: 50 mg kg^{-1} as $(NH_4)_2HPO_4$ and $(NH_4)_2SO4$
P: 300 mg kg^{-1} as $Ca(H_2PO_4)_2.H_2O$ and $(NH_4)_2HPO_4$
K: 100 mg kg^{-1} as KH_2PO_4
S: 15 mg kg^{-1} as $(NH_4)_2SO_4$
Mo: 0.1 mg kg^{-1} as $Na_2MoO_4.2H_2O$
B: 0.5 mg B kg^{-1} as H_3BO_3

The incubation of the soils was continued at the same conditions as above for another three weeks.

Thirty seeds of barley (*Hordeum vulgare* L. 'Rodeo') were placed 1.5 cm below the soil surface in the pot. To minimize evaporation, the soil surface was covered with a 2-cm depth of silica sand which was purified by soaking in 1 M HCl for one week and rinsed with distilled water until no Cl^- was

detected. Germination took place two days after planting. The plants were thinned after one week to seven plants per pot. The pots were weighed every second day for the first two weeks for each cut and then daily for the remainder of the experiment to estimate the water loss. This water was replaced with deionized water. Nutrient solutions were added two days after each of the first and second cut. The crops were harvested at two different growth periods corresponding to Feeke's stages 3 and 6 by cutting 1-cm above soil level. Before cutting of the third cut, all the pots were watered to a moisture content of 30%. Soil samples of 300 g were taken out and placed in plastic bags which were frozen at -5°C until analyses of soil solution chemistry.

The experimental design for the responses of barley shoots was a randomized complete block, two factorial with three treatments times three pH's as main plots and two cuts as subplots. There were eighteen treatments altogether. Three replicates were employed for each treatment.

Plant tissue analysis

The harvested plant material was placed in paper bags and dried at 70°C in a forced-air oven for 72 hours to constant weights and then ground with a stainless steel mill to pass through a 40 mm mesh screen for chemical analyses. 250 mg of samples were wet ashed in 5 ml H_2SO_4 plus H_2O_2 (Thomas *et al*, 1967) for N, P, Ca and K determinations. Calcium and K were determined by atomic absorption spectrophotometry. Total N was determined by the indophenol blue method (Ferrari, 1960) on an autoanalyser. Total P was determined by the vanadomolybdate method (Colwell, 1965) on an autoanalyser.

Soil solution extraction

The immiscible displacement technique with tetrachloroethylene (C_2Cl_4, density 1.6 $g.ml^{-1}$) as described by Kinniburgh and Miles (1983) and Kittrick (1983) was used to obtain samples of the soil solution. One hundred and sixty grams of soil at a moisture content of 30% (w/w, 94% of the field capacity) were divided into four 40-g portions and placed into 50-ml polypropylene centrifuge tubes and 20 ml of C_2Cl_4 was added.

The samples were centrifuged at a speed of 270,000 $m.s^{-2}$ for 30 minutes on an IEC B-20A ultracentrifuge at a constant temperature of 5°C. The aliquots were then transferred to 15-ml plastic assay tubes. The tubes were centrifuged again at a speed of 1,000 rpm for 10 minutes by a MSE GT-2 table centrifuge to completely separate the soil solution from the C_2Cl_4. The soil solution was then collected with a 5-ml hypodermic syringe from the assay tubes and filtered through Whatman No. 42 filter paper and then Millipore 0.22 μm filters and stored in plastic vials in a refrigerator until analysis.

Ortho-phosphate in solution was determined by the ammonium molybdate-ascorbic acid method (Murphy and Riley, 1962), total phosphorus by an ICP-AE spectrometer, dissolved organic carbon (DOC) by the phenolphthalein indictor method (Technicon, 1976).

Results and discussion

Plant yields and P uptake

The results for plant yields and contents of %P, %N and %K in the barley shoots are shown in Table 1 and 2 for Feeke's stages 3 and 6, respectively.

Table 1. Yields (mg pot^{-1}) and chemical composition of plants at Feeke's 3 stage

pH	Treatment	Rep	Yield	% N	% P	% K
5.3	Incorporated	1	1.962	4.75	0.553	6.24
		2	1.482	4.99	0.572	6.13
		3	1.607	4.51	0.534	6.34
	Surface	1	1.612	4.94	0.579	7.07
		2	1.838	4.82	0.617	7.14
		3	1.971	4.51	0.597	6.75
	Control	1	1.283	4.41	0.557	6.59
		2	1.482	4.41	0.557	6.60
		3	1.682	4.41	0.557	6.58
6.5	Incorporated	1	1.972	4.76	0.530	6.30
		2	1.533	4.97	0.578	6.13
		3	1.497	4.56	0.483	6.47
	Surface	1	1.689	4.79	0.638	6.96
		2	1.890	5.01	0.636	6.88
		3	2.102	4.67	0.596	6.85
	Control	1	1.487	5.00	0.610	6.45
		2	1.492	4.97	0.628	6.99
		3	1.709	4.54	0.601	6.56
7.4	Incorporated	1	2.067	4.74	0.517	6.90
		2	1.582	4.85	0.520	5.83
		3	1.155	4.80	0.518	6.36
	Surface	1	1.797	4.98	0.562	6.87
		2	1.309	4.81	0.546	6.72
		3	1.582	4.64	0.530	6.58
	Control	1	1.517	4.59	0.567	6.49
		2	1.399	4.56	0.606	6.91
		3	1.310	4.58	0.536	6.70

Table 2. Yields (mg pot^{-1}) and chemical composition of plants at Feeke's 6 stage.

pH	Treatment	Rep.	Yield	% N	% P	% K
5.3	Incorporated	1	12.16	1.58	0.309	3.38
		2	12.04	1.63	0.363	3.53
		3	12.10	1.40	0.275	3.12
	Surface	1	9.03	1.69	0.209	2.60
		2	12.41	1.38	0.313	3.64
		3	11.80	1.33	0.297	3.53
	Control	1	7.25	1.29	0.382	4.06
		2	6.88	1.25	0.326	3.73
		3	7.79	1.28	0.382	3.86
6.4	Incorporated	1	15.48	2.12	0.371	3.67
		2	15.33	1.99	0.358	3.26
		3	14.15	1.90	0.332	3.84
	Surface	1	14.57	1.79	0.357	3.89
		2	15.13	1.87	0.354	3.59
		3	15.91	1.99	0.312	3.38
	Control	1	10.95	1.55	0.447	4.27
		2	10.95	1.44	0.302	3.59
		3	12.06	1.52	0.429	4.54
7.5	Incorporated	1	16.06	2.25	0.316	3.45
		2	14.08	2.60	0.323	3.40
		3	13.53	2.65	0.333	3.77
	Surface	1	16.11	2.58	0.324	3.17
		2	14.10	2.45	0.343	3.91
		3	16.10	2.23	0.300	3.46
	Control	1	14.66	1.76	0.380	4.04
		2	12.39	2.08	0.337	3.73
		3	14.28	2.06	0.361	3.93

All statistical analyses were performed using a two way analysis of variance (ANOVA) Duncan multiple range test using a 5% probability. The results of these analyses and the average values of the measured plant parametres are shown in Table 3.

Table 3. Average values for plant parameters at Feeke's 3 and 6 stages and ANOVA analysis.

	Feeke 3			Feeke 6		
	Incorporated	Surface	Control	Incorporated	Surface	Control
			% P			
pH 5.3	0.553	0.598	0.557	0.316	0.273	0.363
6.4	0.530a	0.623b	0.613b	0.353	0.341	0.393
7.5	0.518	0.546	0.536	0.324	0.322	0.359
			% N			
pH 5.3	4.75	4.76	4.41	1.67	1.47	1.27
6.4	4.76	4.82	4.84	2.08a	1.88a	1.50b
7.5	4.80a	4.81a	4.57b	2.50a	2.42a	1.97b
			% K			
pH 5.3	6.24a	6.98b	6.58c	3.34	3.26	3.88
6.4	6.30b	6.90a	6.67ab	3.59	3.62	4.13
7.5	6.36b	6.72a	6.70a	3.54	3.51	3.90
			Plant Yield (mg pot^{-1})			
pH 5.3	1.68	1.81	1.48	12.1a	11.1a	7.3b
6.4	1.67	1.89	1.56	15.0a	15.2a	11.3b
7.5	1.60	1.56	1.41	14.6	15.4	13.8

Feeke's stage 3

The highest average yields of barley shoots were obtained for the surface applied treatment at the two lower pH's but the yields for all treatments were not significantly different from each other at $p > 0.05$. Average percentage phosphorus contents were highest in the surface applied treatment but were only significantly different at $p > 0.05$ at pH 6.4 for the incorporated residue treatment. Results for percentage nitrogen showed that at pH 7.5 both residue treatments had significantly higher contents than the control and that for percentage potassium both the control and the surface applied treatment had significantly higher contents than the incorporated residue treatment.

Feeke's stage 6

There were no significant differences in the percentage phosphorus or potassium in any of the treatments. However percentage nitrogen contents for both surface applied and incorporated residue treatments were significantly different at the two higher pH values from those of the control plants (Figure 1). The lowest plants yields were always those of the control and at pH 5.3 and 6.4 were significantly different from the two residue treatments (Figure 2).

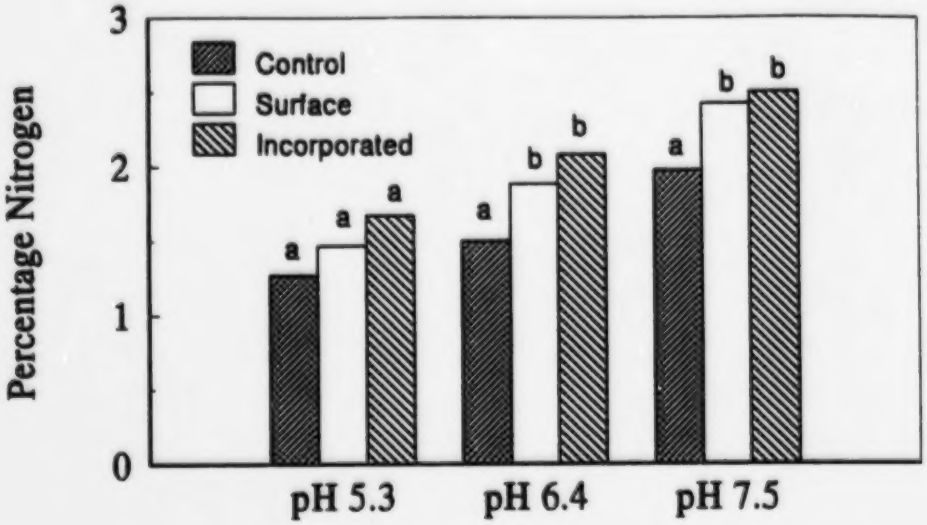

Figure 1. Average percentage nitrogen contents at Feeke's 6 stage.

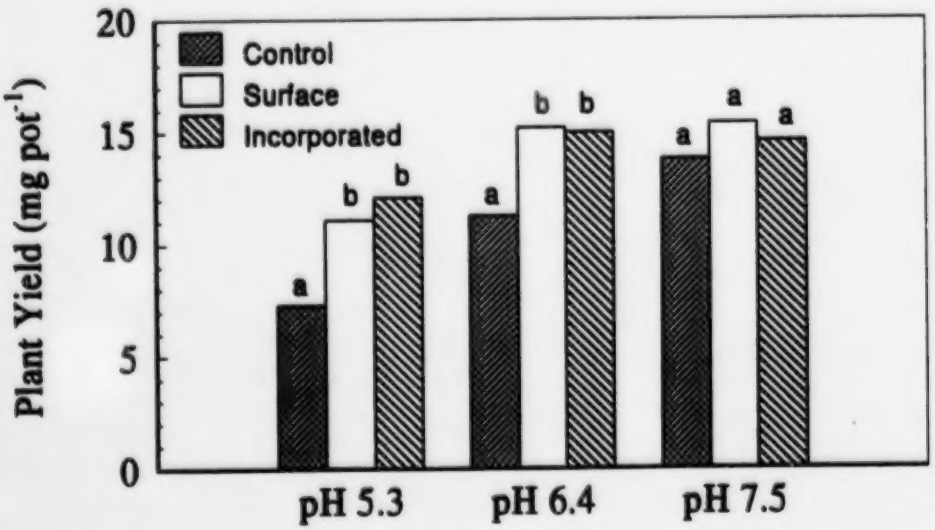

Figure 2. Average plant yields (mg pot^{-1}) at Feeke's 6 stage

Forms of available phosphorus and soluble carbon in soils

Average values of the three replicates for soil test extractable phosphorus, orthophosphate, total soluble phosphorus and soluble carbon are shown in Table 4, together with the results of the ANOVA analyses. The results for the individual replicates are shown in Tables 5 and 6 for Feeke's stages 3 and 6, respectively.

Table 4. Average values for soil parameters at Feeke's 3 and 6 stages and ANOVA analysis.

	Feeke 3			Feeke 6		
	Incorporated	Surface	Control	Incorporated	Surface	Control
	Soluble carbon (ppm)					
pH 5.3	325ab	358a	284b	411a	322b	285b
6.4	301	339	266	356b	363b	256a
7.5	327ab	261a	287b	473a	409b	375b
	Total soluble P (ppm)					
pH 5.3	1.27	1.03	0.91	1.00a	0.74b	0.54b
6.4	0.79	0.65	0.60	0.47	0.50	0.48
7.5	0.71	0.81	0.64	0.69	0.64	0.64
	Ortho-phosphate (ppm)					
pH 5.3	0.092	0.065	0.037	0.065	0.030	0.060
6.4	0.047	0.051	0.055	0.031	0.051	0.048
7.5	0.061	0.113	0.065	0.110	0.048	0.092
	Soil Test Extractable (ppm)					
pH 5.3	46.3	37.8	38	32	33.5	32.2
6.4	33.0	35.2	34.3	29	28.5	29.5
7.5	44.3a	36.7b	40 ab	39.7	33.5	31.8

At Feeke's stage 3, average values for total soluble phosphorus in the extracted soil solutions were higher in the two residue treatments than in the control but in no case were the contents significantly different. At the Feeke's stage 6, the content of soluble phosphorus in the incorporated residue treatment was significantly higher than the other two treatments at the lowest pH of 5.3. At the two higher pH's the contents of soluble phosphorus were almost the same. Contents for ortho-phosphate were extremely variable and no significant differences were recorded for any of the treatments.

Table 5. Forms of P and soluble carbon at Feeke's stage 3

pH	Treatment	Rep.	Soil Test	Total P	Ortho-P	Org.-P	Carbon
5.3	Incorporated	1	49	1.40	0.09	1.15	302
		2	44	1.81	0.03	0.67	330
		3	46	0.61	0.16	0.65	344
	Surface	1	38.5	0.67	0.07	0.61	392
		2	38	0.96	0.06	0.90	367
		3	37	1.45	0.07	1.38	317
	Control	1	49	1.24	0.04	1.37	302
		2	34	0.71	0.02	1.79	269
		3	31	0.81	0.06	0.55	281
6.4	Incorporated	1	34	0.64	0.03	0.61	329
		2	33	1.22	0.03	1.18	286
		3	32	0.51	0.07	0.44	288
	Surface	1	35.5	0.71	0.09	0.62	355
		2	35.5	0.56	0.04	0.53	369
		3	34.5	0.68	0.02	0.66	292
	Control	1	33	0.69	0.05	0.63	208
		2	32	0.47	0.02	0.45	297
		3	38	0.63	0.09	0.54	293
7.5	Incorporated	1	42	0.32	0.04	0.28	338
		2	44	0.83	0.04	0.79	355
		3	47	1.03	0.10	0.93	238
	Surface	1	38	1.16	0.21	0.96	387
		2	31	0.71	0.05	0.67	331
		3	41	0.56	0.08	0.48	367
	Control	1	41	0.38	0.02	0.36	249
		2	37	0.86	0.15	0.71	325
		3	42	0.68	0.03	0.65	287

Table 6. Forms of P and soluble carbon at Feeke's stage 6

pH	Treatment	Rep.	Soil Test	Total P	Ortho-P	Org.-P	Carbon
5.3	Incorporated	1	36	1.22	0.03	1.19	449
		2	30.5	0.98	0.10	0.88	419
		3	29.5	0.81	0.07	0.74	365
	Surface	1	37.5	0.52	0.04	0.48	338
		2	33.5	0.78	0.02	0.76	311
		3	29.5	0.32	0.02	0.30	331
	Control	1	33	0.76	0.07	0.71	294
		2	28	0.99	0.07	0.92	245
		3	35.5	0.46	0.04	0.42	315
6.4	Incorporated	1	33	0.52	0.04	0.48	380
		2	29	0.31	0.02	0.29	332
		3	25	0.58	0.03	0.55	356
	Surface	1	33	0.40	0.04	0.46	347
		2	26	0.44	0.05	0.39	383
		3	26.5	0.67	0.06	0.61	361
	Control	1	28.5	0.50	0.03	0.47	229
		2	31.5	0.47	0.07	0.40	266
		3	28.5	0.46	0.04	0.42	272
7.5	Incorporated	1	39.5	0.78	0.08	0.70	464
		2	42.5	0.46	0.08	0.38	360
		3	37	0.82	0.17	0.65	495
	Surface	1	37.5	0.54	0.06	0.48	418
		2	32	0.57	0.05	0.52	456
		3	32	0.80	0.04	0.76	404
	Control	1	33	0.50	0.10	0.40	367
		2	36.5	0.83	0.11	0.72	410
		3	26	0.60	0.07	0.53	349

Soluble carbon contents at Feeke's stage 3 were significantly lower at pH 5.3 in the control soil than in the surface applied residue treatment, but this effect changed with increasing pH so that at pH 7.5 the incorporated residue treatment had a significantly higher soluble carbon content than the surface applied residue. At Feeke's stage 6 the incorporated residue treatment had a significantly higher soluble carbon content than the control at every pH and was higher than the surface applied treatment at the higher and lower pH's respectively.

There were no significantly differences in the soil test values for any of the treatments for either of the Feeke's stages, although values for soil test phosphorus were lower after the longer growing period at Feeke's stage 6.

Conclusions

There were yield differences between the control and the two residue treatments but these differences were not significant at the first harvesting period at Feeke's stage 3. Final yields at the later harvesting at Feeke's stage 6 were significantly lower in the control than in the two residue treatments at the two lower pH values but the effect of the residue treatments on final barley yields disappeared in the soil limed to a pH of 7.5.

Contrary to initial expectations the increased yield for the residue treatments did not appear to be due to an increased content of tissue phosphorus. The increased plant yields appeared to be more directly related to increased tissue potassium content at the earlier date of harvesting (Feeke's stage 3) and to an increased tissue nitrogen content at the later harvesting date (Feeke's stage 6).

These increased yields also corresponded to increased soluble carbon contents in the extracted soil solutions and therefore it is possible the degradation of the corn residues either at the soil surface or directly incorporated into the soil released soluble nitrogen and potassium. Although there was some evidence for increased soluble phosphorus contents in the extracted soil solutions, these increases were not significant at a probability of less than 5% using the Duncan's multiple range test.

2. Incubation of Corn and Alfalfa Residues with Soil

Experimental Design:-

1 Soil:	Welland clay (Niagara area)		
3 pH's:	1) 5.3 2) 6.4 3) 7.5		Soils limed with various rates of $CaCO_3$ and incubated for 1 month
9 Sampling dates:	1) 1 day 2) 2 days 3) 4 days 4) 8 days 5) 12 days	6) 16 days 7) 24 days 8) 32 days 9) 48 days	
2 Residue types:	1) Alfalfa - low C:N 2) Corn - high C:N		
1 Residue rate:	1) Alfalfa - 0.25 g residue / 100 g container 2) Corn - 0.35 g residue / 100 g container		
1 Residue placement:	- incorporated		
1 Rate of phosphorus addition:	- 20 kg/ha		

All incubations to be performed in triplicate.

Materials and methods

100 g soil were incubated in 150 ml plastic containers with either corn or alfalfa residues as outlined above, with appropriate controls included. At the pre-determined sampling dates 4x25 g soil samples were placed in 50 ml centrifuge tubes and the equilibrium soil solutions extracted by immiscible displacement with tetrachloroethylene. Organic carbon was determined by an auto-analyzer technique and ortho-phosphate determined by the molybdate blue method. Total phosphorus was determined by ICP-AE spectrometry.

Results and Discussion

Corn

The three soil parameters measured in the incubation experiments were total organic carbon, $[C]_T$, total phosphorus, $[P]_T$, and ortho-phosphate, $H_2PO_4^-$ and/or HPO_4^{2-}. These constituents were extracted from soil incubated with corn residues at different time intervals by an immiscible displacement technique. Results for the three parameters are shown in Table 7 and illustrated in Figures 3, 4 and 5.

Table 7. Soil solution carbon and phosphorus ($\mu g\ ml^{-1}$) released during incubation of corn residue at three different pH's.

	Day								
	1	2	4	8	12	16	24	32	48
	---------- Organic carbon ----------								
pH 5.3	321	133	1041	683	945	1763	1118	628	437
6.4	559	509	1041	982	1338	1278	1187	326	143
7.5	959	436	1497	1118	1102	2962	1895	466	253
	---------- Total phosphorus ----------								
pH 5.3	0.330	0.423	0.097	0.095	0.164	0.333	0.185	0.129	0.095
6.4	0.334	0.368	0.115	0.090	0.136	0.184	0.099	0.081	0.076
7.5	0.330	0.390	0.146	0.108	0.246	0.538	0.319	0.161	0.099
	---------- Ortho-phosphate ----------								
pH 5.3	0.669	0.489	0.078	0.029	0.028	0.095	0.032	0.029	0.028
6.4	0.526	0.391	0.187	0.044	0.026	0.073	0.044	0.021	0.020
7.5	0.524	0.476	0.245	0.087	0.035	0.080	0.128	0.125	0.067

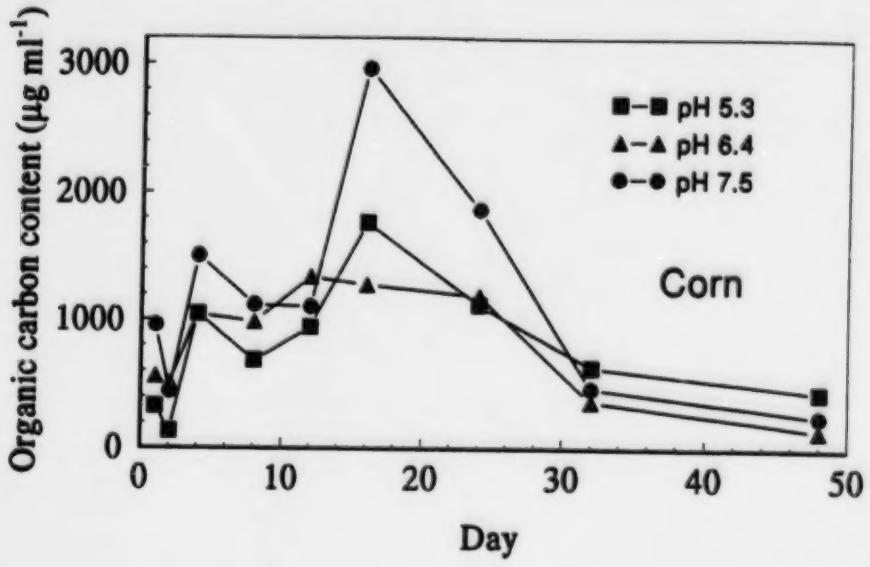

Figure 3. Release of soluble organic carbon, $[C]_T$, from corn residues incubated with soil.

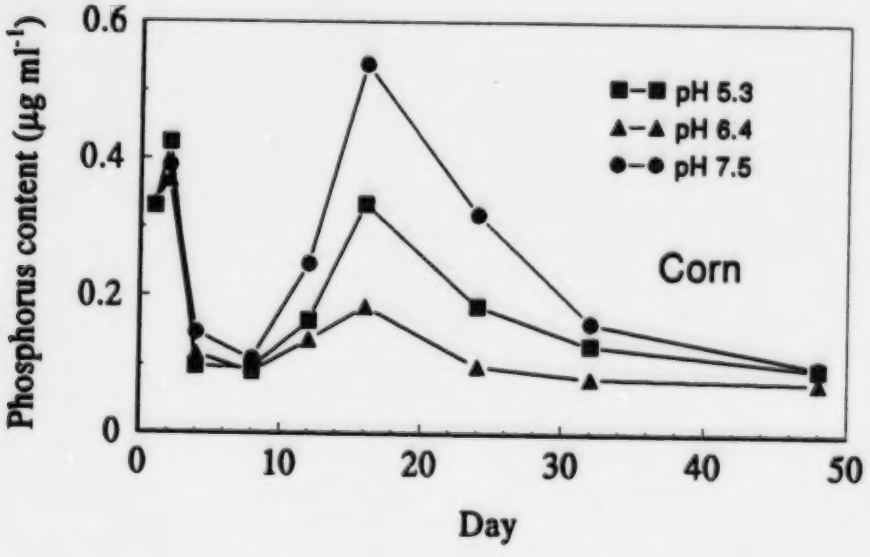

Figure 4. Release of soluble phosphorus, $[P]_T$, from corn residues incubated with soil.

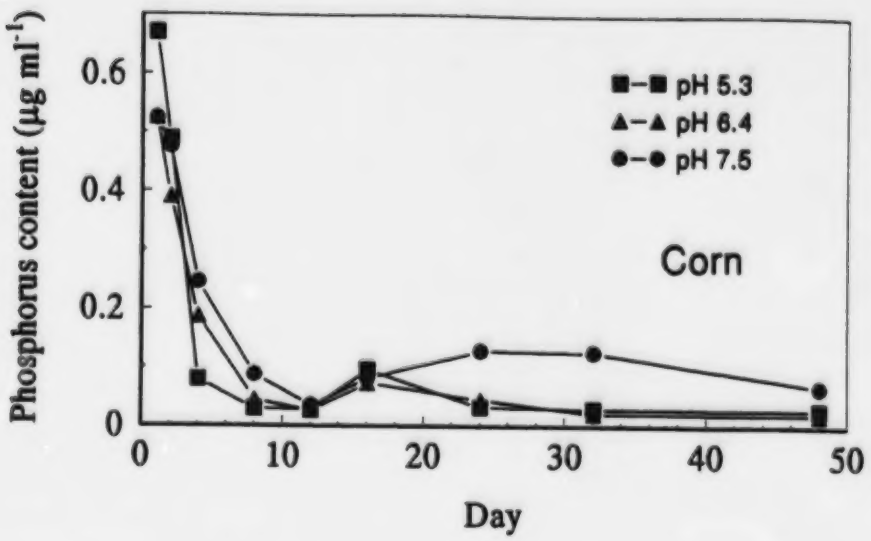

Figure 5. Release of ortho-phosphate from corn residues incubated with soil.

Organic carbon contents increased with time at all three pH values to reach a maximum at about sixteen days and then declined steadily in content to values reach values at forty eight days close to those at the beginning of the incubation experiment (Figure 3). Contents of organic carbon were highest for the soil limed to a pH value of 7.5 followed by the soil at a pH of 5.3 and lastly by the soil with the intermediate pH of 6.4.

The content of total soluble phosphorus as measured by the ICP-AE spectrometer followed a very similar pattern to that of organic carbon, with again contents of total phosphorus reaching a maximum at about sixteen days from the start of the incubation (Figure 4). The relative contents of phosphorus as a function of soil pH also behaved in a manner similar to soluble organic carbon with the lowest amounts of soluble phosphorus being determined in the soil limed to the intermediate pH of 6.5. At forty eight days contents of soluble phosphorus appeared to have reached an equilibrium value which was similar for all the three soils.

Contents of ortho-phosphate decreased sharply from relatively high initial values to low values after about ten days of incubation. In a manner similar to both soluble total carbon and phosphorus contents of ortho-phosphate increased slightly at sixteen days for the soils with pH's of 5.3 and 6.4 to decrease again to the end of the experiment at forty eight days. For the soil with the highest pH ortho-phosphate contents remained relatively high at twenty four and thirty two days before deceasing in content.

Alfalfa

Results for total organic carbon, $[C]_T$, total phosphorus, $[P]_T$, and ortho-phosphate, $H_2PO_4^-$ and/or HPO_4^{2-} are shown in Table 8 and illustrated in Figures 6, 7 and 8.

Table 8. Soil solution carbon and phosphorus ($\mu g\ ml^{-1}$) released during incubation of alfalfa residue at three different pH's.

	Day								
	1	2	4	8	12	16	24	32	48
	---------- Organic carbon ----------								
pH 5.3	1014	1224	1392	1500	2038	1914	2187	1902	1075
6.4	1182	1237	2026	1460	1968	1853	1610	326	143
7.5	1675	1753	2075	1924	2224	2833	2762	1873	992
	---------- Total phosphorus ----------								
pH 5.3	0.375	0.407	0.241	0.298	0.345	1.106	1.158	0.597	0.408
6.4	0.402	0.398	0.256	0.244	0.195	0.524	0.496	0.271	0.122
7.5	0.331	0.551	0.265	0.249	0.310	0.518	0.733	0.435	0.249
	---------- Ortho-phosphate ----------								
pH 5.3	0.198	0.060	0.053	0.026	0.050	0.082	0.094	0.042	0.026
6.4	0.125	0.159	0.057	0.033	0.029	0.057	0.044	0.019	0.013
7.5	0.416	0.406	0.082	0.036	0.081	0.076	0.117	0.036	0.022

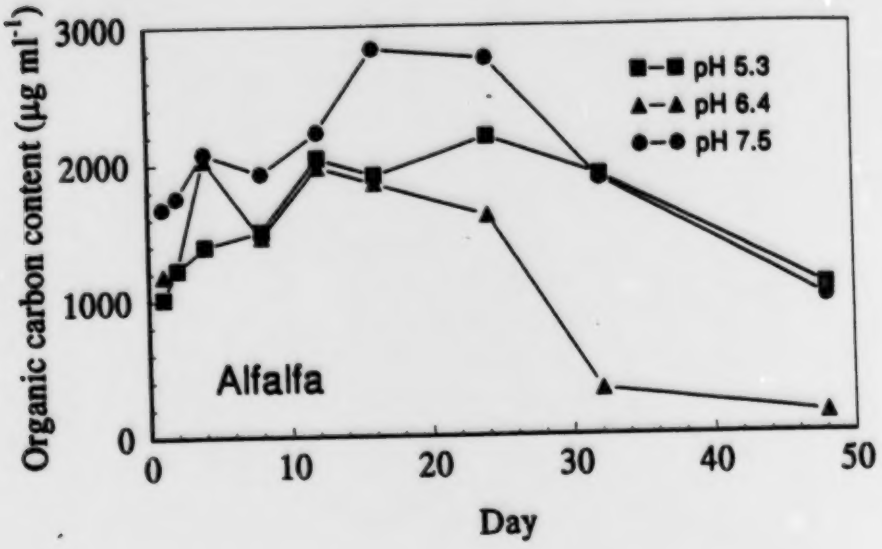

Figure 6. Release of soluble organic carbon, $[C]_T$, from alfalfa residues incubated with soil.

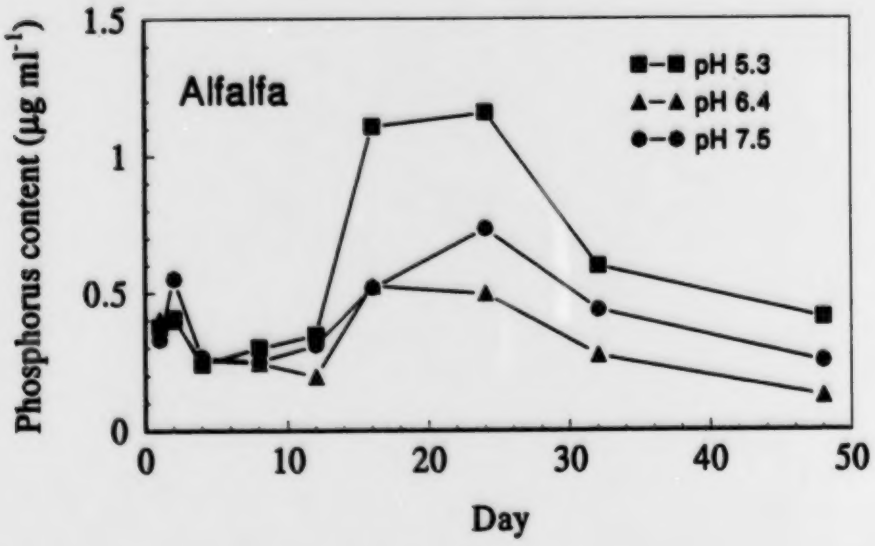

Figure 7. Release of soluble phosphorus, $[P]_T$, from alfalfa residues incubated with soil.

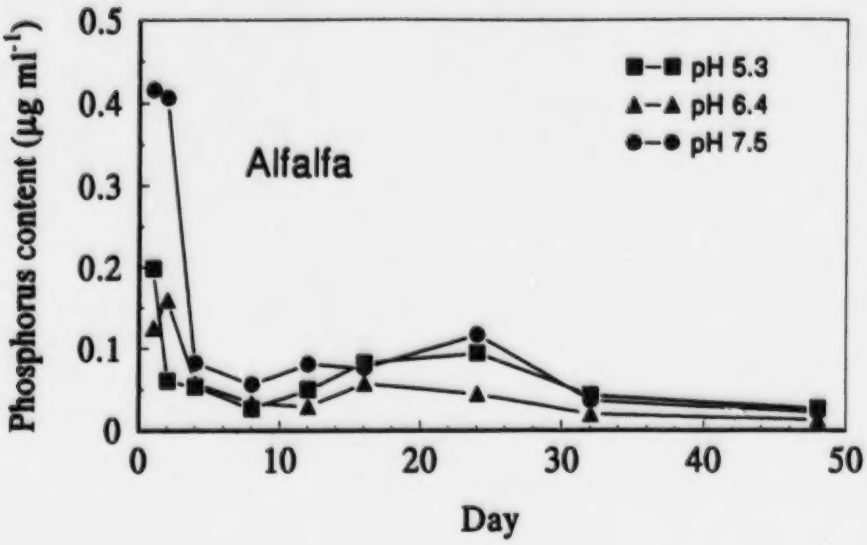

Figure 8. Release of ortho-phosphate from alfalfa residues incubated with soil.

Whereas with corn residues the content of soluble organic carbon declined sharply after sixteen days of incubation, organic carbon released from the degradation of alfalfa residues remained high up to twenty four days before declining (Figure 6). Again lowest contents of organic carbon were released from the residues incubated with the soil at the intermediate pH of 6.4. For the soils at pH's 5.3 and 7.5 contents of soluble carbon remained relatively high even after forty eight days of incubation.

As with the experiments with corn residues, the pattern of release of total soluble phosphorus was very similar to that of organic carbon, with contents remaining high over the period from sixteen to thirty two days (Figure 7). The contents of released total phosphorus were also almost twice as high as those from the soils incubated with corn residues even though the amounts of organic carbon released from both residues were approximately the same.

Contents of ortho-phosphate release from alfalfa were similar to those for corn residues in that there were small but significant increases in ortho-phosphate towards the middle of the incubation period (Figure 8). As with the contents for both organic carbon and total phosphorus, this increase occurred at a later period in the incubation than for incubated corn residues.

Conclusions

Incubating both corn and alfalfa residues with soils at different pH's lead to an increase in soluble organic carbon, soluble total phosphorus and ortho-phosphate. The maximum amounts of each of the constituents occurred at about the some time period, with contents of the constituents being released over a longer time period for alfalfa than for corn. Because of uncertainties in the exact nature of total phosphorus measured by the ICP-AES technique, it is not clear whether this increase in phosphorus content is due to the release of mineral-bound phosphorus or due to an increase in organic phosphorus.

3. Phosphate Adsorption in the Presence of Organic Acids

Experimental design:-

1 Soil: Welland clay (Niagara area)

3 pH's: 1) 5.3
2) 6.4
3) 7.5

Soils limed with various rates of $CaCO_3$ and incubated for 1 month

6 Rates of phosphorus addition ranging from 0.05 to 0.5 mM

7 Organic acids:
1) salicylic acid
2) citric acid
3) oxalic acid
4) phthalic acid
5) p-hydroxybenzoic acid
6) acetic acid
7) catechol

Methods and materials

100 mg of soil were shaken overnight in 50 ml centrifuge tubes with 20 ml of the appropriate solutions containing P and/or 10^{-3} M organic acids in 0.01M $LiClO_4$. The final concentrations of phosphate were 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 mM. The amounts of phosphorus remaining in solution were determined by an autoanalyzer technique using the procedure described previously. The amount of phosphorus adsorbed was calculated as the difference between the amounts of phosphorus added and that remaining in solution.

Results and Discussion

Phosphorus adsorption in the absence of organic acids

The amount of phosphorus adsorbed, q, in relation to the amount remaining in solution, c, is shown in Figure 9. As expected, for all three soil pH's the amount of phosphorus adsorbed approached a maximum as the amount of phosphorus in solution increased. The greatest amount of retention was found for the soil having the highest pH value of 7.5, with the lowest amount of retention found in the soil with the intermediate pH of 6.4.

The adsorption for all three soils conformed to the Langmuir adsorption isotherm with regression coefficients for c/q against c ranging from 0.98 to 0.99 for the three soils. Calculated adsorption maxima, q_{max}, were 10.18 for the soil with unadjusted pH of 6.4, 9.78 for the unlimed soil and 22.1 mmol kg^{-1} for the soil limed to a pH of 7.5. The adsorption maxima were calculated from the linearized form of the Langmuir adsorption isotherm.

$$c/q = c/q_{max} + 1/k \cdot q_{max}$$

where k is a coefficient related to the extent of bonding.

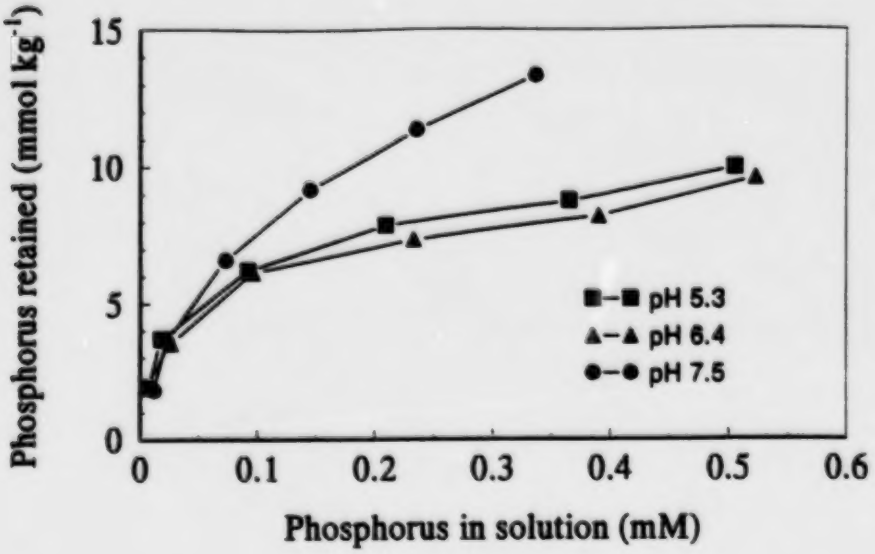

Figure 9. Adsorption isotherms for phosphorus adsorption in the absence of organic acids.

Effect of organic acids on phosphorus retention

The acids chosen for study all form complexes, to a greater or lesser extent, with the same soil surfaces as applied phosphorus and can thus compete for the same adsorption sites, so reducing the retention of phosphorus by soil. The organic acids can be grouped as follows:-

Strongly complexant - citric and oxalic acids
Moderately complexant - salicylic and phthalic acids and catechol
Weakly complexant - acetic, p-hydroxybenzoic and acetic acids.

As many of the acids behaved similarly for all three pH's, only representative results have been presented. All the organic acids reduced the extent of phosphorus adsorption for each of the pH's studied when compared to the control soils which did not contain any organic acids. The results for the soil with a pH of 5.3 is typical of the results obtained for the other two soils and is shown in Figure 10. The highly complexant ligand, oxalic acid, together with the other strongly complexant ligand, citric acid, had the greatest effect on reducing the extent of adsorption of phosphorus. Although results have only been shown for acetic and phthalic acids, the other weakly complexant ligands, salicylic acid, p-hydroxybenzoic acid and catechol, behaved almost identically to acetic and phthalic acids and did not have as great an effect on phosphorus retention as oxalic and citric acids.

The extent of the effect of the organic acids on decreasing phosphorus retention was always greatest for the soil with the highest pH of 6.5 and the least for the most acidic soil with a pH of 5.3. Typical results for acetic acid, catechol and phthalic acid are shown in Figures 11, 12 and 13, respectively.

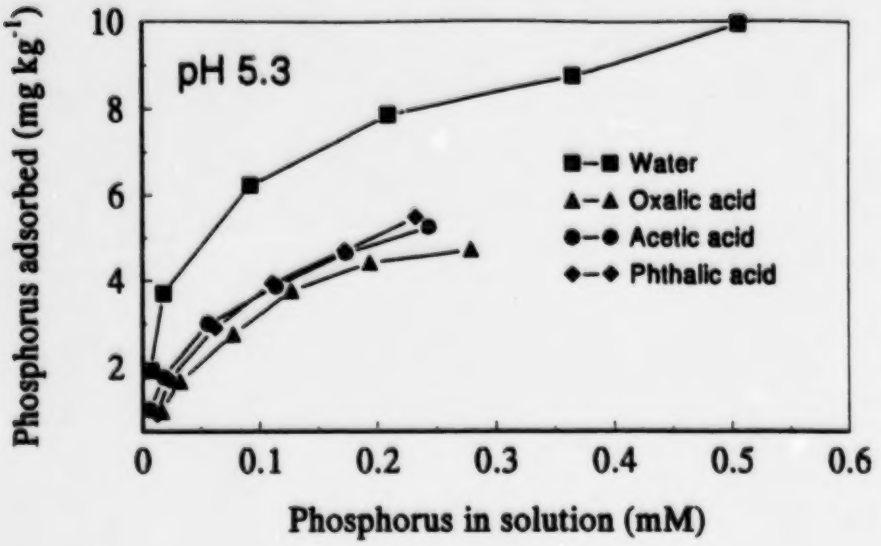

Figure 10. Effect of organic acids on reducing phosphate retention

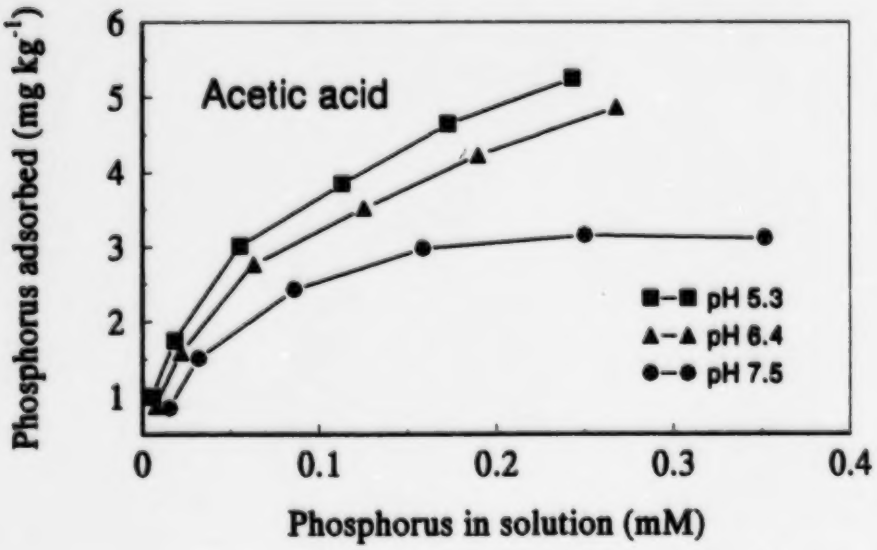

Figure 11. Effect of acetic acid on phosphate adsorption of pH 5.3, 6.4 and 7.5.

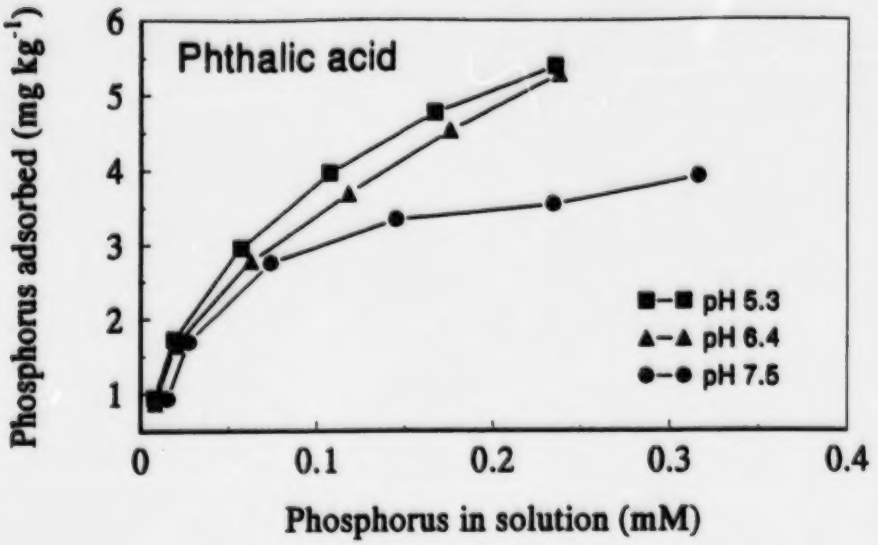

Figure 12. Effect of phthalic acid on phosphate adsorption of pH 5.3, 6.4 and 7.5.

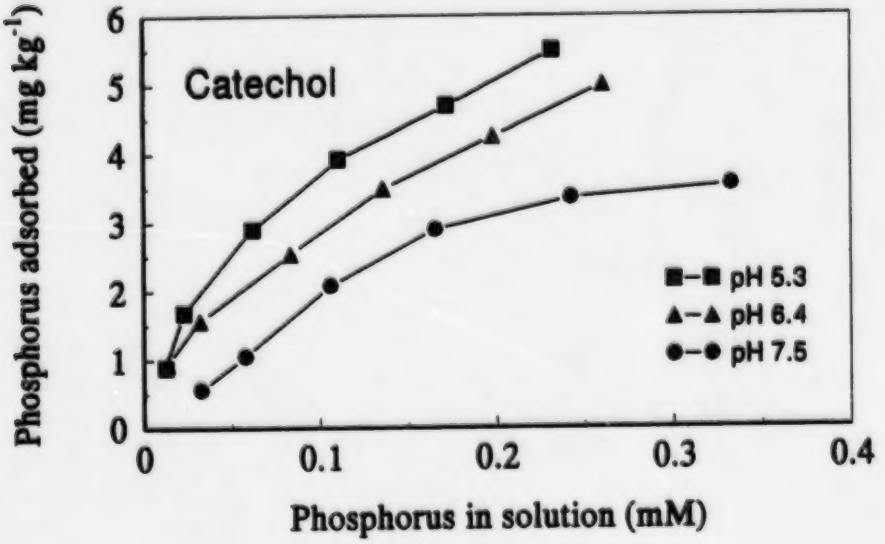

Figure 13. Effect of catechol on phosphate adsorption of pH 5.3, 6.4 and 7.5.

Conclusions

Organic acids are formed as a result of the decomposition of applied crop residues and these acids may decrease the extent of adsorption of applied phosphate by complexing with the same sites on soil particles as phosphorus. Results from this study demonstrate that the effect is greatest for the highly complexant acids such citric and oxalic acids and that the effect was greatest at higher pH's.

GENERAL RESULTS AND DISCUSSION

There were differences in the yield of barley between the control soil and the two residue treatments - surface applied and incorporated corn residue. These differences in yield however were not significant at the first harvesting period, that is at Feeke's stage 3. Final yields at the later harvesting at Feeke's stage 6 were significantly lower in the control than in the two residue treatments at the two lower pH values but the effect of the residue treatments on final barley yields disappeared in the soil limed to a pH of 7.5.

The increased yield for the residue treatments did not appear to be due to an increased content of tissue phosphorus. The increased plant yields appeared to be more directly related to increased tissue potassium content at the earlier date of harvesting (Feeke's stage 3) and to an increased tissue nitrogen content at the later harvesting date (Feeke's stage 6).

The increased yields also corresponded to increased soluble carbon contents in the extracted soil solutions and therefore it is possible that the degradation of the corn residues either at the soil surface or directly incorporated into the soil released soluble nitrogen and potassium, in addition to soluble phosphorus. Although there was some evidence for increased soluble phosphorus contents in the extracted soil solutions these increases were not significant at a probability of less than 5% using the Duncan's multiple range test.

Incubating both corn and alfalfa residues with a soil limed to different pH's lead to an increase in soluble organic carbon, soluble total phosphorus and ortho-phosphate. The maximum amounts of each of the constituents occurred between two to three weeks, with contents of the constituents being released over a longer time period for alfalfa than for corn. Because of uncertainties in the exact nature of total phosphorus measured by the ICP-AES technique, it was not clear whether this increase in phosphorus content is due to the release of mineral-bound phosphorus or due to an increase in organic phosphorus.

By incubating the soils with phosphate in the presence and absence of different naturally occurring organic acids. It was shown that retention of phosphorus was less in the presence of these acids and that those organic acids that form strong bonds with the surfaces of soil particles were the most effective in reducing specific adsorption of phosphate.

This study has shown that there is an increase on crop yield if soils at three different pH's are amended with crop residues either applied at the soil surface or incorporated into the soil. Incubation of the soils with either corn or alfalfa residues increases the amount of soluble phosphorus in the soil solution after about two to three weeks of incubation. With increased time however the content of soluble phosphorus decreases. This increase in soluble phosphorus is probably due in part to release of inorganically and organically bound phosphorus in the residues and, as the final part of the study has shown, to release of soil bound phosphorus by an increased concentration of released organic acids.

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APPENDIX I

DETERMINATION OF DISSOLVED ORGANIC PHOSPHORUS IN SOIL SOLUTIONS BY AN IMPROVED AUTOMATED PHOTO-OXIDATION PROCEDURE

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Summary

An improved automated photo-oxidation procedure to determine dissolved organic phosphorus in soil solutions is described. Organically combined phosphorus is converted quantitatively to orthophosphate under UV radiation and an excess of dissolved oxygen. The orthophosphate is determined spectrophotometrically using the Murphy and Riley (1962) procedure, modified by increasing the concentration of ascorbic acid. Fluoride was added to the system to overcome potential interference when working with soil solutions. The limit of detection was 0.64 $\mu g\ L^{-1}$ PO_4^{3-}-P and calibration was linear over the range studied (5-1000 $\mu g\ L^{-1}$ PO_4^{3-}-P).

Acknowledgments

This method was developed partly at Guelph and partly in Aberdeen by M.D. Ron Vaz, A.C. Edwards and C.A. Shand of the Plants Division, Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen, UK and M. Cresser of the Department of Plant and Soil Science, University of Aberdeen, Aberdeen, UK.

Introduction

An autoanalyzer technique involving ultra-violet irradiation to destroy organic-metal constituents and subsequent colorimetric determination of released metals has recently been developed for Al and Fe (Jensen and Evans, 1992). This method provides a means of determining water soluble inorganic- and organic-bound elements as well as dissolved organic C. The objective of the proposed study was to develop a simple and efficient method of phosphorus which embodies the principal concepts developed for organic- and inorganic Al and Fe. This method should allow a differentiation of operationally definable organic and inorganic species of phosphorous in water extracts of soil, in soil solutions and in drainage waters.

Current schemes for the autoanalyzer determination of water-soluble carbon and for phosphorus have been developed by Technicon (1978) and by EPA (1979). For carbon of water extract of soil is acidified and oxidized with potassium persulphate and ultra-violet irradiation. The manifold used for organic C is essentially that given in Technicon (1978) and that for phosphorus given in U.S. EPA (1979). By taking the waste stream from the carbon manifold and introducing it into the phosphorus manifold the organic compounds in the sample will have been completely digested in the carbon manifold and organic-phosphorus released into solution can now be determined in the phosphorus manifold.

Determination of water-soluble phosphorus with and without ultra-violet radiation and chemical oxidation should result in a quantitative estimate for inorganically-bound plus organically-bound metal. Organically-bound phosphorus is determined as the difference between the two measurements. At the same time an aliquot of the CO_2 generated from the digestion of the organic C present in the sample is dialysed through a silicone rubber membrane and diffused into a weakly buffered phenolphthalein indicator solution. The decrease in colour of the indicator is proportional to the original C concentration.

Fractionation of solution phosphorus

A scheme that can distinguish between operationally definable fractions that include inorganic colloids and water-soluble organically- and inorganically-bound phosphorus species is present in Figure 1. The fractionate scheme combines quantification by the autoanalyzer techniques presented below and methods for the determination of total phosphorus.

Total phosphorus (P_T) in soil solutions or water extracts can be determined by Inductively Coupled Plasma Atomic Emission spectrometry (ICP-AES). As organically-bound phosphorus is released by acid digestion and ultra-violet treatment, the measurement of total water-soluble phosphorus (P_{sol}) determined after passage through the carbon manifold and the phosphorus manifold is comprised of both inorganically-bound phosphorus originally present in the solution and that released from the oxidation of organically-bound phosphorus.

The content of organically-bound phosphorus (P_{org}) can then be calculated by subtracting total water-soluble phosphorus (P_{sol}) measured after ultra-violet treatment from the water-soluble phosphorus (P_{inorg}) that was determined prior to sample ultra-violet irradiation treatment. Estimates of inorganic colloidal phosphorus (P_{col}) are obtained by subtraction of the water-soluble phosphorus (P_{sol}) from total phosphorus (P_T).

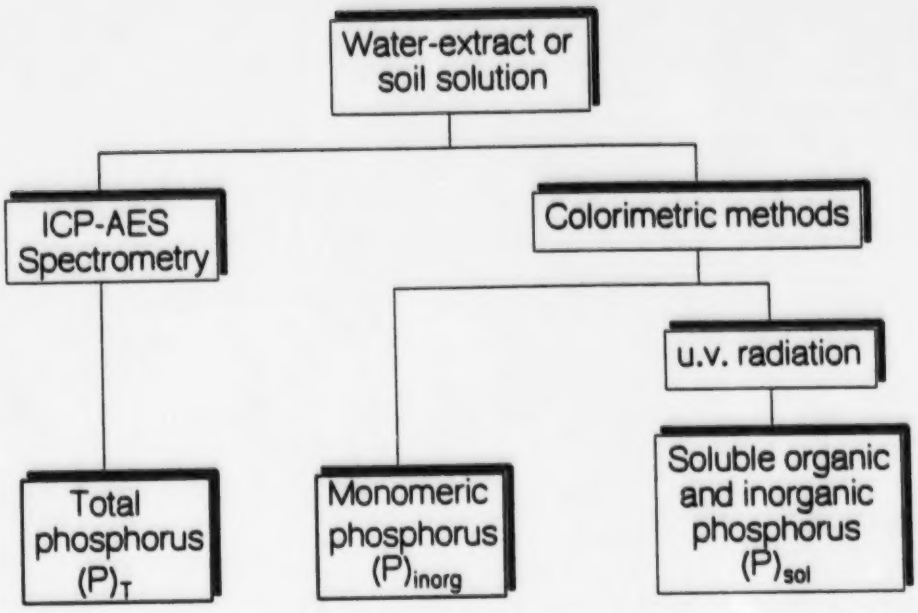

Figure 1. Analytical scheme for speciation of phosphorus.

Experimental

The manifold developed is shown in Figure 2. It was set up taking into consideration the required mixing volume ratios, colour development time and the need for thorough mixing of samples and reagents. Mixing coils used were 15-turn and 45-turn respectively (20 mm coil diameter, 2 mm i.d.); the delay coil was 22-turn (165 mm coil diameter, 2 ml i.d.).

The UV irradiation system consisted of a 50-turn silica coil (32 mm coil diameter, 1 mm i.d.) irradiated by a UV-Lux tube. Orthophosphate determination in irradiated samples was carried out using a procedure modified from Murphy and Riley (1962) The absorbance of the phosphomolybdenum blue was measured at 880 nm using a 50-mm flow cell. The difference in values for irradiated and non-irradiated sample (UV lamp on and off) gave the amount of dissolved organic P present in the sample.

Reagents

All aqueous solutions were prepared using milli-Q ultra purewater. Unless otherwise indicated, all reagents were AnalaR grade or equivalent.

Fluoride : 1.105 g NaF in 100 ml water.

Saturated Potassium Persulphate:

6.4 g $K_2S_2O_8$ in 100 ml water. Warm to dissolve, and allow to cool to room temperature; stand to allow some crystallisation, otherwise it will crystallise in the manifold tube.

Mixed Reagent :

(a) Potassium antimonyl tartrate solution:
Dissolve 0.2908 g $K(SbO)C_4H_4O_6^{-1/2}H_2O$ in 100 ml water.

(b) Ammonium molybdate solution:
Dissolve 12 g $(NH_4)_6Mo_7O_{24}$-$4H_20$ in 250 ml water.

(c) Sulphuric acid, H_2SO_4, 2.5M:
Dilute 148 ml conc H_2SO_4 to 1l with water.

Mix (a), (b) and (c) thoroughly and make up to 2l with water. This reagent must be kept in a dark cupboard.

Ascorbic Acid :

Dissolve 11 g $C_6H_8O_6$ in 250 ml water and add 150 µl of aerosol 22 as wetting agent. This solution is stable for about 1 week at 4°C in the dark.

Phosphorus model compounds

A range of phosphorus compounds found in natural waters was analysed by the proposed method to quantify individual responses to the method. The compounds studied were potassium dihydrogen phosphate, trimetaphosphate trisodium salt, tetrasodium pyrophosphate, α-D-glucose-1-phosphate, β-glycerophosphate, phytic acid, 2-aminoethylphosphonic acid, adenosine-2'(3')- phosphoric acid monohydrate, nicotinamide adenine dinucleotide (reduced form), adenosine-5'-triphosphoric acid disodium dihydrogen salt (general purpose reagent grade).

Working standard solutions of these compounds were prepared in the range of 5-1,000 µg L^{-1} P by dilution of the stock solutions. All the solutions were stored at 4°C to minimize risk of microbial growth.

Results and discussion

Colour development

The automated method consists of two stages:

(1) Photo-oxidation of the sample; the sample is exposed to UV radiation in the presence of an oxidising agent. Organically-bound phosphorus is released as inorganic phosphate.

(2) Determination of DRP; by the spectrophotometric determination as a reduced phosphomolybdate complex in acid solution after irradiation of the sample.

Addition of fluoride

When soil solution samples were run through the system, following synthetic standards, a decrease in the peak heights for the next batch of standards run after the samples was observed. Thus

running the samples resulted in a source of phosphorus removal, possibly via contamination of either manifold tubes and/or of the silica coil. Manifold tubes were replaced but the loss of phosphorus was still observed indicating that the silica coil was contaminated.

The possible explanation for this source of phosphorus loss could be aluminium interferenceand hence addition of fluoride eleiminated this problem.

The stability of the colour developed in the modified phosphomolybdenum blue reaction in the presence of a large amount of fluoride was studied. No differences in absorbance values occurred, but it was found that the rate of reaction decreased in the presence of fluoride. A delay coil was incorporated into the manifold to give around 12 min colour development time which was sufficient to reach maximum absorbance.

Linearity and Limit of Detection

The recovery of phosphorus from different phosphorus compounds was measured using the proposed method. Firstly, 200 $\mu g\ L^{-1}$ P solutions of each compound were run using the autoanalyzer procedure with the UV lamp off to ensure that the analytical response for DOP was not due to DRP impurities. The same solutions were run with UV lamp on and without persulphate, and with UV lamp on with persulphate. The results showed that complete recovery was achieved for simple organic phosphorus compounds. Furthermore, total recovery was achieved without using persulphate, which means that UV radiation, in addition to the dissolved oxygen present either from the air bubbles or in the water, was enough to release organic phosphorus bound in the ester form (phytic acid, α-D-glucose-1-phosphate, β-glycerophosphate, adenosine-2'(3')-phosphoric acid), or via a C-P bond (2-aminoethylphosphonic acid). The complex chemical nature of phosphorus containing organic compounds likely to be encountered in soil solution requires the use of persulphate to ensure complete photo-oxidation.

The linearity of the automated procedure was checked. The range studied was from 5 to 1,000 $\mu g\ L^{-1}\ PO_4^{3-}$-P. The calibration shows good linearity over this range ($r^2 = 0.9999$, Peak height (mm)= -9.14 + 2.12[$\mu g\ L^{-1}$ P]). Limit of detection (defined as the analyte concentration giving a signal equal to the blank signal, y_B plus three standard deviations of the blank, s_B) was 0.64 $\mu g\ L^{-1}$ P which could be improved using a 50 mm flow cell. The final configuration of the organic phosphorus manifold is shown in Figure 2.

Conclusion

The detection limit obtained with the proposed procedure, 0.64 $\mu g\ L^{-1}$, was substantially better than the limit of 10 $\mu g\ L^{-1}$ obtained by McKelvie *et al.* (1989). Such a low detection limit was necessary for analysis of some of the soil solution samples studied. A satisfactory and simple procedure has been found for overcoming interference from aluminium. The segmented flow system obviates the need for adding a high pH sodium tetraborate buffer to absorb evolved carbon dioxide.

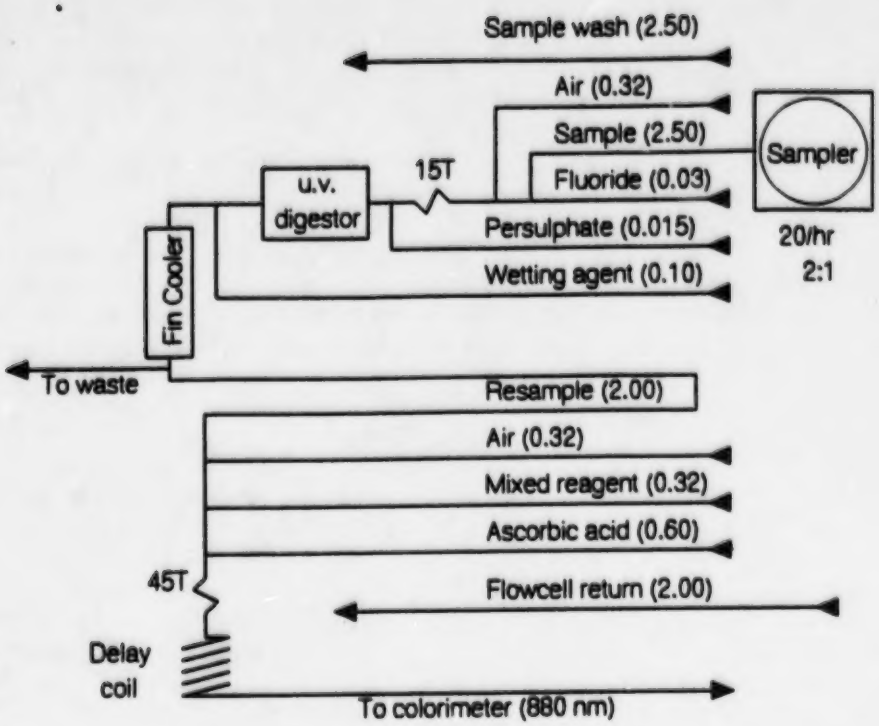

Figure 2. Auto-analyzer manifold for the determination of organic and inorganic phosphate.

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